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Historical perspective on: Quantum yield of chlorine-atom formation in the photodissociation of chlorine peroxide (ClOOCl) at 308 nm [Volume 173, Issue 4, 12 October 1990, Pages 310–315]

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ABSTRACT

The original letter concluded that chlorine peroxide (ClOOCl) photolizes in the atmosphere to yield free chlorine atoms. Some later work questioned the experimental results, but subsequent papers clearly established the validity of the original findings.

Summary by Mario Molina, Nobel prize-winner: Professor Mario J. Molina

This Letter describes experimental work concluding that chlorine peroxide (ClOOCl) photolizes in the atmosphere to yield free chlorine atoms. Previous work by our group had suggested that this compound would play a key role in the destruction of stratospheric ozone in the polar stratosphere; it is an intermediate in a catalytic cycle in which chlorine monoxide radicals, produced by the reaction of chlorine atoms with ozone, recombine to yield chlorine peroxide, with photolysis regenerating the free chlorine atoms.

The chlorine peroxide molecule, which is unstable at room temperature, had just been identified in the laboratory by our group as well as by others. The hypothesis to be tested was that photolysis of this compound would yield free chlorine atoms rather than two chlorine monoxide radicals, which would be the case if the weakest bond broke in the process. Instead, the hypothesis was that absorption of radiation around 300 nm would involve the transition to an upper repulsive state of a non-bonding electron localized on the chlorine atom.

Although subsequent laboratory work basically confirmed the results summarized in our Letter, another Letter published years later described laboratory results appearing to contradict the main conclusion of our Letter, thus questioning the idea that the Antarctic ozone hole was indeed caused by the decomposition products of industrial CFCs by means of a well-understood chemical mechanism. This situation led to additional laboratory studies of the photolysis of chlorine monoxide, which conclusively established that the ozone destruction mechanism we had proposed earlier in our Chemical Physics Letters paper was indeed the correct one.

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